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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> A01N 57/20 // (A01N 57/20 A01N 25:14, 25:12)	<b>A1</b>	<b>(11) International Publication Number:</b> WO 92/12637 <b>(43) International Publication Date:</b> 6 August 1992 (06.08.92)
<b>(21) International Application Number:</b> PCT/US92/00274 <b>(22) International Filing Date:</b> 15 January 1992 (15.01.92)  <b>(30) Priority data:</b> 645,365                      24 January 1991 (24.01.91)    US 804,592                      13 December 1991 (13.12.91)    US  <b>(71) Applicant:</b> MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).  <b>(72) Inventors:</b> PRILL, Erhard, John ; 1215 Lockett Lane, Kirk- wood, MO 63122 (US). RICHARDSON, Ronald, Owen ; 1231 Field Avenue, Ellisville, MO 63011 (US).  <b>(74) Agent:</b> BOLDING, James, Clifton; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).		<b>(81) Designated States:</b> AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European pa- tent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European pa- tent), JP, KP, KR, LK, LU (European patent), MC (Eu- ropean patent), MG, ML (OAPI patent), MN, MR (OA- PI patent), MW, NL (European patent), NO, PL, RO, RU, SD, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> IMPROVED GLYPHOSATE FORMULATIONS  <b>(57) Abstract</b>  This invention relates to agriculturally acceptable compositions containing N-phosphonomethylglycine for use in killing or controlling weeds, to a method for killing or controlling weeds and to a process for preparing these compositions. The compositions are dry and water soluble and comprise N-phosphonomethylglycine, an acid acceptor and optionally a solid or liquid surfactant.		

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IMPROVED GLYPHOSATE FORMULATIONSField of the Invention

This invention relates to a substantially dry  
5 agriculturally acceptable composition(s) containing N-  
phosphonomethylglycine or a salt thereof, to a use of  
such a composition(s) in killing or controlling weeds  
and to a process for preparing such a composition(s).

10 Glyphosate (N-phosphonomethylglycine) is well  
known in the art as an effective herbicide. Glyphosate,  
an organic acid, is only slightly soluble in water.  
Glyphosate is typically commercially formulated and  
applied as a water-soluble salt, especially as the  
15 isopropylamine salt (IPA salt).

Various formulations of glyphosate, salts of  
glyphosate, methods for preparing salts of glyphosate,  
and methods of use thereof are disclosed in U.S. Patents  
20 3,799,758 and 4,405,531 issued to John E. Franz on March  
26, 1974 and September 20, 1983 respectively. Other  
U.S. patents which disclose salts of glyphosate include  
U.S. Patent 4,315,765 issued to George B. Large on  
February 16, 1982; U.S. Patent 4,507,250 issued to Izhak  
25 Bakel on March 26, 1985; U.S. Patent 4,397,676 issued to  
Izhak Bakel on August 9, 1983; U.S. Patent 4,481,026  
issued to Michael P. Prisbylla on November 6, 1984; U.S.  
Patent 4,140,513 issued to Erhard J. Prill on February  
20, 1979.

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Hungarian Patent Application No. 431/88 assigned to Alkaloida Vegyeszet discloses that water soluble plant-growth controlling solid active agents, N-phosphonomethylglycine and its derivatives are mixed with  
5 carbonate and hydrogen carbonate salts and with customary plant protection additives. Sufficient initiating water is added to govern the extent of a double decomposition reaction between these compounds. The solid obtained is converted by colloid-chemical  
10 means into foams, creams, moist pastes and wet feel powders packaged as powders, granules or compressed briquettes.

European Patent Application 0 127 773 A1 assigned  
15 to Wellcome Foundation Limited, published 12/12/84 discloses a pesticidal composition comprising a pesticide, an emulsifier or dispersing agent for the pesticide, and a self-disintegrating agent capable of effervescing or swelling on being contacted with water.  
20 The composition is disclosed as being conveniently in the form of an effervescent pesticidal tablet.

UK Patent Application GB 2 095 556 A published October 6, 1982 discloses a composition for controlling  
25 the presence of unwanted microorganisms comprising a probiocide that produce the biocide formaldehyde, an effervescent couple for evolving carbon dioxide and optionally a surfactant.

UK Patent Specification 1 505 738 assigned to Kirby Pharmaceutical Limited, published March 30, 1978 discloses a process for the preparation of a water  
30 soluble chemical composition compounded in an effervescent tablet form, which comprises the direct pressing into tablet form by a direct compression  
35 process of a powder comprising a chemical compound, an alkali metal bicarbonate, an alkali metal carbonate and

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a solid, water soluble aliphatic carboxylic acid or an acid salt thereof.

UK Patent Specification 1 516 682, assigned to  
5 SOGEMARIC, published July 5, 1978 discloses a mixture of one or more active phytosanitary materials (herbicides, growth regulators, insecticides, fungicides) in solid form, i.e. either the active material alone if it is solid, or impregnated on a solid, inert support if it is  
10 liquid, is mixed with the additives, wetting agents, dispersants of the type commonly used in the production of wettable powders, and with the non-hydrophilic filler and the disintegrating agent described therein. The mixture is homogenized and then compressed into tablets  
15 or pellets of the required shape under a pressure in the range from 50 to 1000 kg/cm<sup>2</sup> and preferably under a pressure in the range from 100 to 600 kg/cm<sup>2</sup>.

DuPont PCT/US89/0272 discloses a tablet  
20 consisting essentially of about 20 to 75% of a pesticide melting about 100°C and having a water solubility of no more than about 5% and a delivery system consisting essentially of a dibasic or tribasic organic carboxylic acid, ammonium or alkali carbonate or bicarbonate,  
25 dispersant, PVP and an anionic or nonionic wetting agent whereby the dispersion of the pesticide in water is fine enough to pass a 50 mesh screen.

Ciba Geigy AU-A-53042/90 discloses a pesticidal  
30 active ingredient concentrate in effervescent tablet form which disintegrates in water to form a sprayable suspension and consists essentially of a water insoluble active ingredient, surface-active agents, fillers and binders, flow regulators and a disintegrator, which  
35 concentrate contains the disintegrator in the form of an effervescent granulate comprising potassium carbonate and or potassium hydrogen carbonate, a solid water

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soluble acidic substance and a finely divided water-insoluble substance capable of binding water.

DuPont EPO published patent application 0 360 441  
5 discloses a water soluble granule and water dispersible granule composition whereby glyphosate is disclosed as a granular substrate along with potassium carbonate.

Ciba Geigy AU-A-25886/88 discloses effervescent  
10 compressed pesticidal tablets comprising a sulfonyl urea, dispersion agent and a disintegrator further comprising a solid water soluble acidic substance, an alkali/alkaline earth metal/hydrogen carbonate, a  
gliding or flow regulating agent and optionally a filler  
15 or binder.

Rhône Poulenc Published UK Patent specification  
GB 2 104 780 A discloses an effervescent herbicidal granule which is said to be a water soluble granule of  
20 an acid herbicide or plant growth regulator, alkaline carbonate/bicarbonate, impurities from the herbicide acid additives and surfactants or lubricants.

EPO published patent application 0 204 146  
25 discloses a herbicidal composition comprising (a) 2-(4-chloro-2-fluoro-5-propargyloxyphenyl)-5,6,7,8-tetrahydro-1H-1,2,4-triazolo (1,2-s)pyridazine-1,3,-2H-dione (I), with (b) glyphosate (i) glufosinate (ii) bialaphos (iii) and/or paraquat (1,1'-dimethyl-4,4'-bipyridinium  
30 ion) (iv) or their salts and an inert carrier or diluent.

EPO published patent application 0 255 760  
discloses a granule shaped agricultural composition  
35 prepared by introducing to the top of a drying tower, a mixture of the agricultural chemical, an anionic surfactant and optionally one or more additives in the form of a concentrated solution or an aqueous slurry.

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Published Japanese patent applications J62175407 and J62175408 disclose a herbicide containing a solid carrier, additives, and a herbicidal component and  
5 having a particle size of 48-150 mesh. The disclosed herbicidal components are (3-amino-3-carboxy)propyl-1)methyl-phosphonic acid, N-(phosphonomethylglycine, (2-amino-4-methylphosphino-butyril) alanylalanine and their salts.

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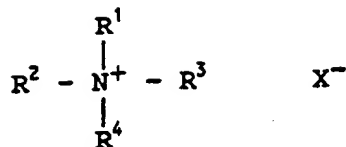
Published European Patent Application 0 206 537 discloses a solid, substantially non-hygroscopic, phytoactive composition comprising an intimate mixture of a phytoactive N-phosphonomethyl-N-carboxymethyl  
15 compound and a surfactant which is solid at ambient temperatures.

Published European Patent Application 0 256 608 discloses a method for the preparation of a solid,  
20 phytoactive composition comprising (a) reacting an acid form of a phytoactive N-phosphonomethyl-N-carboxymethyl compound with a liquid amine to form the amine salt of said N-phosphonomethyl-N-carboxymethyl compound (b) admixing said amine salt of said N-phosphonomethyl-N-  
25 carboxymethyl compound with a molten surfactant, the surfactant being solid at ambient temperature and (c) cooling said mixture to a temperature below the melting point of the surfactant to form a composition comprising said surfactant and said amine salt of N-phosphono-  
30 methyl-N-carboxymethyl compound interdispersed in the matrix thereof and which is solid at ambient temperatures.

Publication No. WO 87/04595 discloses a  
35 herbicidal water-soluble dry-particulate glyphosate formulation comprising the sodium salt of glyphosate and a surface active agent having the following formula:



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wherein R<sup>1</sup> and R<sup>2</sup> are independently methyl or ethyl, R<sup>3</sup> is methyl, ethyl, benzyl or C<sub>10</sub> to C<sub>18</sub> alkyl, R<sub>4</sub> is C<sub>10</sub> to C<sub>18</sub> alkyl and X is chloro or bromo.

10

Japanese LOP 145,205-88 discloses an aqueous concentrate herbicidal formulation comprising a water soluble glyphosate salt, ammonium sulfate and a quaternary ammonium salt.

15

PCT/WO8704712 discloses a method of preparing a particulate alkali metal salt of N-phosphonomethylglycine, which comprises adding a solid alkali metal base with agitation to N-phosphonomethylglycine containing up to 25% water.

20

Research Disclosure dated November 1986 discloses in publication 27161 a wettable powder formulation effective in control of weeds comprising N-phosphonomethylglycine, a non-ionic surfactant, diatomaceous earth, an inorganic salt (ammonium sulphate) and an antifoaming agent.

25

Chemical Abstracts 103: 191395k (1985) Glyphosate preparations. Davydov, A.M.; Vechtomova, T.N.; Bazunova, G. G. (USSR). Zashch. Rast. (Moscow) 1985, (9), 40-1(Russ) discloses the 36% aq. soln. Utal (I) [96638-41-4] and the 50% wettable powder Fosulen (II) which are Soviet brands of glyphosate.

30

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#### SUMMARY OF THE INVENTION

The invention comprises a substantially dry, water soluble or dispersible, agriculturally acceptable composition comprising substantially nonreacted N-

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phosphonomethylglycine, an acid acceptor and optionally a solid and/or liquid surfactant, the optional liquid surfactant if present preferably in the range from about 0.2 to about 15.0% by weight surfactant and more preferably in the range of 0.2 to 10.0% by weight surfactant although greater amounts of optional liquid surfactant may be employed depending on other formulation ingredients.

10           The term agriculturally acceptable includes use of compositions of this invention in the homeowner, and apartment areas as well as industrial, residential and other similar areas where use may be convenient.

15           Compositions of this invention optionally further comprise ammonium sulfate, alkali metal sulfates such as potassium sulfate, sodium sulfate, alkali metal chlorides such as potassium chloride, urea, mixtures thereof and the like. The composition may optionally  
20 include a synergist, a quick-burn additive, a humectant, a co-herbicide, a dye, a pigment, a corrosion inhibitor, a thickener, a dispersing agent, a calcium sequestrant, mixtures thereof and the like.

25           In a process for preparing the composition of this invention, the substantially dry, water soluble, agriculturally acceptable composition is prepared by admixing substantially unreacted N-phosphonomethylglycine and an acid acceptor, and optionally a solid or  
30 liquid surfactant, optionally with pulverized ammonium sulfate and thereafter blending, tableting, compacting, briquetting, or granulating, such as by wet extrusion, these illustrative ingredients and optional ingredients to form a composition(s) of this invention.

35

#### Objects of the Invention

It is an object of this invention to provide a dry, water soluble, agriculturally acceptable glyphosate

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composition for use including the homeowner and residential market.

It is an object of this invention to provide a process for preparing a dry, water soluble powder or granular agriculturally acceptable composition optionally containing a surfactant.

It is yet another object of this invention to provide a herbicidal method of use for killing and controlling weeds using a substantially dry, water soluble, agriculturally acceptable composition.

It is a further object of this invention to provide the substantially dry, water soluble, agriculturally acceptable formulation which can be transported at a lower cost, which has increased content of herbicidally active ingredients (N-phosphonomethylglycine, acid acceptor, optional surfactant), which can be mixed with various co-herbicides in compatible fashion to form a storage stable composition and which can be packaged, (combustible or recyclable or disposable) containers if desired and which is easy to use.

25

These and other objects are achieved in this invention which is hereinafter described in more detail.

#### Detailed Description of the Invention

30

The invention comprises a substantially dry, water soluble, (preferably powder or granular) agriculturally acceptable composition comprising N-phosphonomethylglycine, an acid acceptor and optionally a solid or liquid surfactant.

35

If prepared as a substantially dry material as for example a powder, illustratively the powder is typically less than about minus 50 mesh and contains in

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the range from about 0.01% weight to about 10.0% weight and preferably less than about 2% weight percent water but more than about 0.2%, although greater or lesser amounts of moisture may be present depending on the formulation ingredients selected.

If desired, a defoamer, a corrosion inhibitor, a thickener, a dispersing agent, a calcium sequestrant, a synergist, a quick burn down additive, a humectant, a co-herbicide, a dye or a pigment may be admixed individually or collectively in the composition.

Certain co-herbicides which form water soluble salts may be used if desired. Such co-herbicides may be selected from the group consisting of 2,4-D (2,4-dichlorophenoxyacetic acid), dicamba (3,6-dichloro-o-anisic acid), picloram (4-amino-3,5,6-trichloro-pyridine-2-carboxylic acid), MCPA (4-chloro-o-tolyloxyacetic acid), dalapon (2,2-dichloropropionic acid), dichlorprop 2-(2,4-dichlorophenoxy)propionic acid), MCPB (4-[(4-chloro-o-tolyl)oxy]butyric acid), acifluorfen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate), chloramben (3-amino-2,5-dichlorobenzoic acid), endothall (7-oxabicyclo(2.2.1)-heptane-2,3-dicarboxylic acid), mecoprop ([2-(2-methyl-4-chlorophenoxy)propionic acid], 2,4,5-T (2,4,5-trichloroacetic acid), 2,3,6-TBA (2,3,6-trichlorobenzoic acid), glufosinate-ammonium (3-amino-3-carboxypropyl)-methylphosphinate, imazapyr (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid), imazaquin, (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid), bialaphos (DL-homoalanin-4-yl-methyl-phosphinate), mixtures thereof and the like.

If further desired, the co-herbicide salt may be blended in the composition instead of the acid form

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being included in glyphosate and acid acceptor,  
(optional surfactant) composition.

It may be preferred to utilize a solid, water  
5 insoluble co-herbicide in a composition of this  
invention. In that embodiment, the co-herbicide is  
present in the composition as a fine powder:  
sulfonylureas such as sulfometuron-methyl (2-[3-(4,6-  
dimethylpyrimidin-2-yl)ureidosulphonyl]benzoic acid),  
10 and chlorsulfuron (1-(2-chlorophenylsulphonyl)-3-(4-  
methoxy-6-methyl-1,3,5-triazin-2-yl)urea), diuron (N'-  
(3,4-dichlorophenyl)-N,N-dimethylurea) simazine (2-  
chloro-4,6-bis(ethylamino)-5-triazine), metsulfuron-  
methyl (methyl 2-[[[4-methoxy-4-methyl-1,3,5-triazin-  
15 2-yl)amino]-carbonyl]-amino]sulfonyl]benzoate),  
chlorimuron-ethyl (ethyl 2-[[[4-chloro-6-methoxy-  
pyrimidin-2-yl)amino]-carbonyl]-amino]sulfonyl]-  
benzoate), linuron (N-(3,4-dichlorophenyl)-N-methoxy-N-  
methylurea), atrazine (2-chloro-4-(ethylamino)-6-  
20 (isopropylamino)-s-triazine), mixtures thereof and the  
like. It may be desirable to include a dispersing  
agent.

For example, the water insoluble co-herbicide may  
25 also be a liquid or solid present in said composition as  
a water dispersible granule: alachlor (2-chloro-2',6'-  
diethyl-N-methoxymethylacetanilide), acetochlor (2-  
chloro-2'-ethyl-6'-methyl-N-ethoxymethyl-acetanilide),  
atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-  
30 triazine, metolachlor (2-chloro-6'-ethyl-N-(2-methoxy-  
1-methylethyl)acet-q-toluidide), fomesafen (5-[2-  
chloro-4-(trifluoromethyl)phenoxy]-N-(methyl-sulfonyl)-  
2-nitrobenzamide), oxyfluorfen (2-chloro-1-(3-ethoxy-4-  
nitrophenoxy)-4-(trifluoromethyl)benzene), fenoxaprop-  
35 ethyl ethyl 2-[4-(6-chloro-2-benzoxazolyloxy)-  
phenoxy]propanoate), diuron N'-(3,4-dichlorophenyl)-  
N,N-dimethylurea, metsulfuron-methyl, simazine 6-  
chloro-N,N'-diethyl-1,3,5-triazine 2,4-diamine,

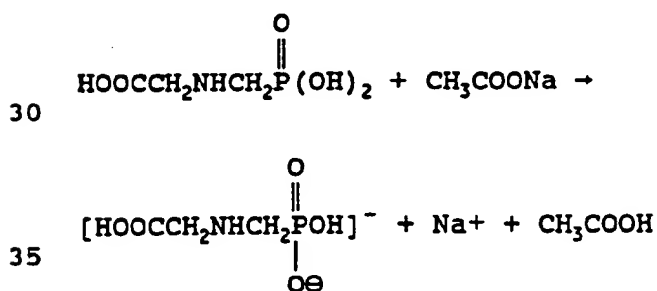
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chlorimuron-ethyl, linuron, chl rsulfuron, sulfometuron-ethyl, mixtures thereof and the like.

Suitable acid acceptors may be illustratively  
 5 selected from the group consisting of ammonium and  
 alkali metal carbonates, bicarbonates, meta borates,  
 acetates, citrates, formates, oxalates, phosphates,  
 propionates, pyrophosphates, metasilicates,  
 10 orthosilicates, sulfites, thiosulfates, tetraborate,  
 monoacid phosphates, tripolyphosphates, metaphosphates,  
 sodium hydroxide, potassium hydroxide, tetrasodium EDTA,  
 mixtures thereof and the like.

In this invention the composition comprises  
 15 substantially nonreacted glyphosate (N-phosphonomethyl-  
 glycine), an acid acceptor and an optionally solid or  
 liquid surfactant. A liquid surfactant can be used if  
 present in small enough quantity or if a large quantity  
 of an additive such as ammonium sulfate is present or if  
 20 adsorbed on a high surface area carrier.

Using sodium acetate as an example of an acid  
 acceptor and without being bound by theory, the  
 following reaction may occur upon dissolving a  
 25 glyphosate/sodium acetate mixture in water.



The pKa's for glyphosate are 2.27, 5.58 and  
 40 10.25. In order for a basic salt to be useful for  
 solubilizing glyphosate, it must be a salt of an acid  
 with a pKa somewhat greater than 2.27. Also, unless it

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precipitates as a fine solid, e.g. oxalic acid, the acid should be water soluble. The pKa values for a number of acids and the equivalents of base available from their salts (i.e. sodium, potassium, ammonium, etc.) for  
5 solubilizing glyphosate are provided in Table I.

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TABLE 1

ACID	pKa	Equivalents of Base Available*
acetic	4.75	1
boric	9.00	1
carbonic	6.36, 10.25	2
citric	3.08, 4.47, 5.40	3
EDTA		2**
formic	3.75	1
glycolic	3.83	1
lactic	3.08	1
oxalic	1.23, 4.19	1
phosphoric	2.12, 7.21, 12.67	2
propionic	4.87	1
pyrophosphoric	0.85, 1.49, 5.77, 8.22	2
m-silicic	9.7, 12.0	2
o-silicic	9.66, 11.70, 12.00, 12.00	4
succinic	4.16, 5.61	2
sulfurous	1.81, 6.91	1
tartaric	3.22, 4.82	2
thiosulfuric		2
tetraboric	ca 4, ca 9	2

\* To solublize glyphosate of a salt such as sodium, potassium, ammonium, amine, etc.

\*\* Only two equivalents of base can be utilized because EDTA and its mono- and disodium salts have very low water solubility



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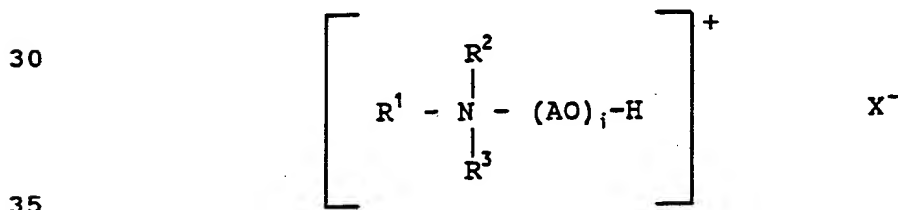
Suitable surfactants (optional) include nonionic surfactants, anionic surfactants, cationic surfactants and amphoteric surfactants, mixtures thereof and the like, preferably ones that provide increased herbicidal activity of N-phosphonomethylglycine or its salts.

Examples of optional nonionic surfactants are polyoxyethylene polyoxypropylene block copolymers, polyoxyethylene alkyl phenols, polyoxyethylene oleyl ethers, alkylglycosides, mixtures thereof and the like.

Examples of optional anionic surfactants are sodium lauryl sulfate, sodium mono- and di- alkyl naphthalene sulfonates, sodium alpha-olefin sulfonates, sodium alkylbenzene sulfonates, sodium alkane sulfonates, mixtures thereof and the like, including sodium, potassium and amine salts.

Examples of optional cationic surfactants are ethoxylated fatty amines and their corresponding quaternary salts such as ethoxylated tallowamines, ethoxylated oleylamines, ethoxylated cocoamines and ethoxylated soyamines, mixtures thereof and the like.

Examples of other optional cationic surfactants include propoxylated quaternary ammonium surfactants. Such surfactants can have the formula:

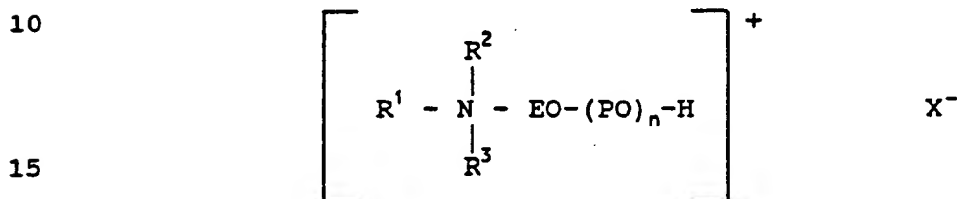


wherein A or each A represents an alkylene group having 2 or 3 carbon atoms, R<sup>1</sup> and R<sup>2</sup> are each independently an alkyl group having from 1 to 5 carbon atoms; R<sup>3</sup> is an alkyl group having from 1 to 5 carbon atoms or a group having the formula (AO)<sub>i</sub>-H; i (in a compound in which R<sup>3</sup>

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is an alkyl group) or  $i + j$  (in a compound in which  $R^3$  is a group having the formula  $(AO)_j-H$ ) has a value of from 2 to 20; and  $X^-$  is a suitable anion.

- 5 A preferred composition of the invention comprises a glyphosate herbicide and a quaternary ammonium compound the latter having a structure represented by the formula:



- wherein -EO- is an ethylene oxide radical and -PO- is a propylene oxide radical,  $R^1$  and  $R^2$  are each independently an alkyl group having from 1 to 3 carbon atoms;  $R^3$  is an alkyl group having from 1 to 3 carbon atoms, a group having the formula  $(EO)_m-H$  or a group having the formula  $EO-(PO)_m-H$ ;  $n$  (in a compound in which  $R^3$  is an alkyl group) or  $n + m$  (in a compound in which  $R^3$  is a group having the formula  $EO-(PO)_m-H$ ), has a value of from 2 to 20; and  $X^-$  is a suitable anion and  $n$  and  $m$  are each independently varying integers.

- 30 Examples of optional suitable amphoteric surfactants are Monaterics, Miranols, betaines, Lonzaines, mixtures thereof and the like.

- Preferable agriculturally acceptable salts of N-  
35 phosphonomethylglycine include the ammonium, isopropylamine, trimethylsulfonium, iminourea salts, sodium, potassium salts, mixtures thereof and the like.

- In another embodiment the composition of this  
40 invention may further comprise ammonium sulfate, potassium sulfate, potassium chloride, sodium sulfate,

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urea, mixtures thereof and the like. If desired, the composition may include a defoamer.

If desired, the composition may further include a synergist, a quick-burn additive, a humectant, a co-herbicide, a dye, a pigment, a dispersing agent, a corrosion inhibitor, a thickener, a calcium sequestrant, a bittering agent, mixtures thereof and the like. The thickener is typically selected from the group consisting of sodium ligninsulfate, starches, cellulose derivatives, high molecular weight polyoxyethylenes, gums, mixtures thereof and the like.

If desired, a dry, water soluble, agriculturally acceptable composition of this invention may be prepared in a process which comprises admixing pulverized ingredients, N-phosphonomethylglycine, acid acceptor, and optional solid or liquid surfactant, optionally with pulverized ammonium sulfate and thereafter blending these ingredients to form said composition. Optionally, the blended ingredients may be pulverized. After the blending operation, wet extrusion may be carried out, followed by an optional drying step.

This invention also includes a method of killing or controlling weeds by applying a herbicidally effective amount of composition of this invention to the locus of the plant or weed to be killed or controlled as prepared if dew is present and the form of a composition of this invention is suitable for example a wettable powder, or preferably by adding diluent water and spraying the diluted composition on the weed.

The preferred shape of a composition of this invention is that of a tablet wherein the tablet is about 2 inches (5.1 cm) long by about 1/2 inch (1.3 cm) wide by about 1/2 inch (1.3 cm) thick although greater or lesser individual measurements and sizes may be

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employed if desired. Th preferred weight is in the range from about 1 to about 36 grams.

Typically a pump-up type or hand trigger sprayer  
5 will be used for applying a diluted composition of this invention to weeds or plants. The sprayer will preferably be filled with about 12 ounces (340 grams) clear water and a tablet comprising a composition of this invention is added. The tablet is left to dissolve  
10 (about 1 to about 3 minutes) and then additional water (about 12 ounces) (340 grams) is added.

The following examples are presented to illustrate the present invention as well as some of the  
15 various embodiments of the inventions. These examples are presented as being illustrative of the novel formulations and herbicidal use and are not intended to be a limitation of the scope of this invention.

20

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EXAMPLESEXAMPLE 1

5           Examples of Water Soluble Powder (WSP)  
formulations with illustrative acid acceptors and using  
an optional surfactant were prepared by blending the  
ingredients which had been previously ground to minus 50  
mesh. An N-phosphonomethylglycine/optional surfactant  
10 weight ratio of 2:1 was used. A higher or lower ratio  
could be used. Five percent excess acid acceptor over  
theory was usually employed. The compositions are shown  
in this Example.

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EXAMPLE 1

<u>ACID ACCEPTOR, WEIGHT %</u>	<u>GLYPHOSATE* Weight %</u>	<u>SURFACTANT** Weight %</u>	<u>SWS-131 Defoamer, Weight %</u>
Trisodium phosphate, 25.75	48.03	Witconate AOS, 26.34	--
Trisodium phosphate, 23.28	47.62	" "	0.05
Potassium oxalate.H <sub>2</sub> O, 53.12	31.31	" "	--
Sodium formate, 21.91	52.15	" "	--
Sodium formate, 21.19	50.43	" "	0.05
Sodium citrate, 28.17	47.95	" "	--
Sodium propionate, 27.50	46.37	" "	0.05
Sodium propionate, 28.39	47.81	" "	--
Sodium tetraborate.10H <sub>2</sub> O, 44.20	37.37	" "	--
Sodium sulfite, 20.63	53.00	" "	--
Sodium sulfite, 19.84	50.98	" "	--
Sodium acetate, 24.48	48.32	" "	0.50
Disodium EDTA.2H <sub>2</sub> O***, 42.53	37.01	" "	--
Tetrasodium EDTA, 42.76	38.23	" "	--
Sodium oxalate, 29.31	47.21	" "	--
Sodium oxalate, 22.15	49.75	" "	0.50
Sodium tetraborate.5H <sub>2</sub> O, 36.63	40.50	" "	0.05
Ammonium acetate, 24.12	50.65	" "	--
Potassium acetate, 28.81	47.53	" "	--
Tripotassium phosphate, 25.55	47.69	" "	0.05

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EXAMPLE 1 ...Continued

<u>ACID ACCEPTOR, WEIGHT %</u>	<u>GLYPHOSATE* Weight %</u>	<u>SURFACTANT** Weight %</u>	<u>SWS-131 Defoamer, Weight %</u>
Sodium carbonate, 17.25	52.65	Witconate AOS	29.10
Sodium carbonate, 17.80	54.24	" "	21.10
Sodium ortho silicate, 15.28	56.48	" AOK	28.24
Sodium meta silicate, 19.30	53.80	" AOS	26.90
Sodium oxalate, 36.26	40.73	" "	22.51
Sodium oxalate, 53.09	29.84	" "	16.57
Sodium hydroxide (76%) 16.04	51.23	Sellogen HR (75%)	32.73
			1.00
			0.95
			--
			--
			0.50
			0.50
			--

\* 99.6% glyphosate used.

\*\* Witconate AOS, a liquid concentrate, was dried and powdered. The percentages given are for the dried material. Witconate AOK is a dry product. The composition of this surfactant can be found in Table II.

\*\*\* EDTA, mono and di-sodium EDTA are insoluble in water; therefore, only two equivalents of tetrasodium EDTA are available for solubilizing glyphosate, EDTA precipitated when disodium EDTA was used as an acid acceptor.

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Water soluble powders (WSP) formulations were prepared for use in bioassay tests to determine the relative contributions of the various acid acceptors to the glyphosate herbicidal activity. The compositions of 5 the WSP formulations are shown in this Example.



EXAMPLE 2FORMULATION COMPOSITIONS

INGREDIENTS	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Glyphosate (99.5%)	50.43	48.32	52.65	50.98	47.62	46.37	47.69	40.50	11.70	13.92	50.47	49.75	40.73	29.84	38.23
Witconate AOK (90%)*	27.88	24.48	29.10	28.18	26.34	25.63	26.26	22.37	6.47	7.70	27.90	27.60	22.51	16.57	19.01
SWS Q-131**	0.50	0.50	1.00	1.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	--
Sodium Formate	21.19								4.92	5.84	9.89				
Sodium Acetate		26.70													
Sodium Propionate						27.50									
Sodium Phosphate					23.28										
Sodium Tetraborate.5 H <sub>2</sub> O								33.63							
T tra sodium EDTA															42.76
Sodium carbonate			17.25												
Sodium sulfite				19.84											
Potassium phosphate								25.55							

EXAMPLE 2 ...ContinuedFORMULATION COMPOSITIONS

INGREDIENTS	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
Sodium xalate											11.23	2.15	36.26	53.09	
Ammonium sulfate									76.42						
Ammonium chloride										72.03					
Glyphosate assay	50.18	48.08	52.39	50.73	47.38	46.14	47.45	40.30	11.64	13.85	50.22	49.73	40.53	29.69	38.04
* Powder form of Witconate AOS															
** Silicon defoamer on an inert carrier															

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EXAMPLE 3

The results of the bioassay test of Example 2 formulations are shown below. Roundup herbicide was used as a comparative of the prior art. Comparing the results of formulation A versus formulation I shows the beneficial effect of ammonium sulfate (AS).

In all of the greenhouse bioassay tests provided in this specification, pot-grown weed species were sprayed with aqueous solutions of the glyphosate WSP formulations using a track sprayer calibrated to apply about 20 gallons/acre (187 liters/hectare) at about 30 psi (21 kilo Pascals).

15

BIOLOGICAL EVALUATION OF SEVERAL WATER-SOLUBLE  
POWDER HERBICIDE FORMULATIONS

	<u>FORMULATION</u>	<u>TREATMENT</u>	<u>% INHIBITION*</u>
20	COMPARATIVE	Roundup Herbicide	52.9
	A	HCOONa	16.3
	B	CH <sub>3</sub> COONa	13.3
	C	Na <sub>2</sub> CO <sub>3</sub>	10.8
	D	Na <sub>2</sub> SO <sub>3</sub>	11.3
25	E	Na <sub>3</sub> PO <sub>4</sub>	14.6
	F	CH <sub>3</sub> CH <sub>2</sub> COONa	14.6
	G	K <sub>3</sub> PO <sub>4</sub>	12.1
	H	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	7.9
	I	HCOONa	
30		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	21.7
	J	HCOONa	
		NH <sub>4</sub> Cl	7.1
	K	(COONa) <sub>2</sub>	15.4
	O	Na <sub>4</sub> EDTA	25.4
35	P	Untreated Check	0

\* The mean of four rates (1/8, 1/4, 1/2 and 1 pounds

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glyphosate/acre) (0.14, 0.28, 0.56 and 1.12 kg/ha) on Johnsongrass as the weed species, four weeks after treatment.

5

EXAMPLE 4

In order to determine the effect of various acid acceptors on glyphosate activity, WSP formulations were prepared without Witconate surfactant. The surfactant was tank mixed into the spray solutions for bioassays.

- 10 Example 5 hereinafter shows the results when surfactant, an ethoxylated tallow amine was used and Example 6, when Witconate AOS was used.

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EXAMPLE 4  
WSP FORMULATIONS WITHOUT SURFACTANT

FORMULATION COMPOSITIONS

INGREDIENTS	A	B	C	D	E	F	G	H	I	J	K	L
Glyphosate (99.5%)	70.41	64.41	74.57	71.99	67.17	62.77	65.11	52.51	62.28	75.47	70.72	47.20
SWS Q-131			1.00									
A. Sodium formate	29.59											
B. Sodium acetate		35.59										
F. Sodium propionate						37.23						
E. Sodium phosphate					32.83							
H. Sodium tetraborate 4H <sub>2</sub> O								47.49				
C. Sodium carbonate			24.43									
D. Sodium sulfite				28.10								
G. Potassium phosphate							34.89					
I. Potassium acetate									37.72			
J. Sodium hydroxide (76%)										24.53		
K. Sodium oxalate											29.98	
L. T trasodium EDTA												52.80
Glyphosate (100%)	70.37	64.38	74.53	71.95	67.14	62.74	65.08	52.48	62.25	75.43	70.68	47.18

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EXAMPLE 5EVALUATION OFWSP FORMULATIONS (ACID ACCEPTORS) USING

5 AN ETHOXYLATED AMINE SURFACTANT HAVING A DEGREE OF  
ETHOXYLATION IN THE RANGE FROM ABOUT 15 TO ABOUT 18

	<u>TREATMENT **</u>	<u>% INHIBITION*</u>
	Isopropylamine salt	
10	of glyphosate	55.2
	Sodium formate	27.5
	Sodium acetate	38.8
	Sodium carbonate	36.7
	Sodium phosphate	56.3
15	Sodium sulfite	47.1
	Sodium propionate	47.9
	Potassium phosphate	62.1
	Sodium tetraborate	30.8
	Potassium acetate	54.2
20	Sodium hydroxide	45.8
	Sodium oxalate	48.3
	Tetrasodium EDTA	37.1
	Untreated Check	0

25

\* On Johnsongrass, mean of four rates (1/4, 1/2, 3/4 and 1 pound glyphosate/acre) (0.28, 0.56, 0.84 and 1.12 kg/ha), 4 weeks after treatment.

30 \*\* 0.25 % an ethoxylated amine surfactant present in all spray solutions.

Comparing the bioassay results with the ethoxylated amine surfactant (Example 5) with those of  
 35 Example 3, shows that the inhibitions are highly surfactant dependent.

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EXAMPLE 6EVALUATION OF WSP ACID ACCEPTORS USING WITCONATE AOS SURFACTANT

<u>TREATMENT****</u>	<u>SJG**</u>	<u>% INHIBITION*</u>	<u>MG***</u>
Isopropylamine salt of glyphosate	49.3		42.8
Sodium Sulfite	36.1		40.6
Sodium propionate	41.7		40.6
Potassium Phosphate	30.0		31.7
Potassium Acetate	28.3		45.6
Sodium Hydroxide	41.3		23.3
Sodium oxalate	54.5		50.0
Tetrasodium EDTA	47.2		35.6
Untreated Check	0		0

\* Mean of 3 rates (1/4, 1/2, 1 pound glyphosate per acre) (0.28, 0.56, 1.12 kg/ha), on Johnsongrass and 3 rates (1/2, 1, 1.5 pound glyphosate/acre) (0.56, 1.12, 1.68 kg/ha) on morning glory.

\*\* Seedling Johnsongrass

\*\*\* Morning glory

\*\*\*\* Sprays containing sodium oxalate and sodium EDTA were best against Johnsongrass, whereas those containing sodium oxalate and potassium acetate were best against morning glory. Thus, the acid acceptor giving the best results depends on the weed species and from other tests (see Examples 5, 6 and 12), the surfactant.

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EXAMPLE 7

Glyphosate WSP formulations were prepared and shown to be water soluble using various surfactants at several ratios to glyphosate.

		<u>WSP WITH DIFFERENT SURFACTANTS</u>				<u>GLYPHOSATE/SURFACTANT RATIO</u>
<u>99.6% GLYPHOSATE NUMBER</u>	<u>%</u>	<u>ACID ACCEPTOR, %</u>	<u>SURFACTANT*, %</u>			
1.	54.95	sodium ortho silicate, 15.38	Witconate AOK (90%) 15.38			4:1
2.	37.59	" " 20.30	" " 42.11			1:1
3.	26.60	" " 14.36	" " 59.04			1:2
4.	48.0	sodium formate, 20.19	Morwet B (75%) 31.73			2:1
5.	48.08	" " 20.19	Morwet DB (75%) 31.73			2:1
6.	51.55	" " 21.65	Morwet EFW (94%) 26.80			2:1
7.	51.55	" " 21.65	Morwet M (96%) 26.70			2:1
8.	50.51	" " 21.21	KAS-10 (90%) 28.28			2:1
9.	50.51	" " 21.21	Witconate NAS-1416 (90%) 28.28			2:1
10.	52.08	" " 21.88	Aerosol OTB 26.04			2:1
11.	50.51	" " 21.21	Witconate KAOS-10 (90%) 28.28			2:1
12.	51.02	" " 20.41	KAOS-12 (90%) 28.28			2:1
13.	46.30	" " 19.44	Igepon T-77 (67%) 34.26			2:1

In all solubility tests the glyphosate/water ratio was 1:30 unless otherwise stated.

\* See Table II for composition of the surfactants.

Comments: Example 3 - surfactant dissolved slowly. Example 9 and 10 solution milky in 60 parts water.  
Example 13 - 60 parts water required.



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Acid herbicides such as picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid), dicamba (3,6-dichloro-o-anisic acid), 2,4-D (2,4-dichloro phenoxy)-acetic acid), Bialaphos, MCPA (4-chloro-o-tolylloxyacetic acid) are especially suitable for WSP package mixes with glyphosate since they can also be solubilized by the acid acceptor as is glyphosate. Optionally, a water soluble salt of the acid actives could be blended with the glyphosate WSP formulation.

10

The compositions of package mix WSPs prepared are found in EXAMPLE 8. Included are the straight package mixes and ones with dicamba (3,6-dichloro-o-anisic acid), 2,4-D (2,4-dichlorophenoxy)acetic acid) and picloram (4-amino-3,5,6-trichloropyridine-2-carboxylic acid) also containing ammonium sulfate, which are common tank mix combinations. A defoamer and an anti-drift agent may also be included. The ratios of ingredients can be varied greatly as long as sufficient acid acceptor is present.

15  
20

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EXAMPLE 8GLYPHOSATE WSP PACKAGE MIXES

<u>CO-HERBICIDE, %</u>	<u>ACID ACCEPTOR, %</u>	<u>99.6% GLYPHOSATE, %</u>	<u>SURFACTANT*, %</u>	<u>AMMONIUM SULFATE, %</u>
Dicamba (88%), 18.54	sodium hydroxide (76%)	12.43 23.85	Witconate AOK, 45.18	---
" "	" "	6.16 11.82	" "	50.43
Dicamba (84%) 26.69	trisodium phosphate,	31.02 28.20	Witconate AOS, 14.09	---
Dicamba (86%) 11.45	sodium tetraborate.10 H <sub>2</sub> O,	33.39 19.91	Witconate AOS 35.25	---
Dicamba (86%), 15.10	sodium hydroxide (76%)	12.14 26.25	" "	---
2,4-D (97%), 28.28	trisodium phosphate	26.33 15.99	" "	---
" "	" "	15.13 7.66	" "	50.07
" "	sodium tetraborate.10H <sub>2</sub> O	46.55 18.68	" "	---
" "	sodium hydroxide (76%)	7.91 10.33	" AOK 19.55	44.07
" "	" "	14.15 18.47	" "	---
Picloram (92%) 1.18	tripotassium phosphate	8.00 8.63	" AOS 4.31	77.88
" "	" "	36.66 38.73	" "	---

\* Witconate AOS is a 39% aqueous product which was dried down and powdered. AOK is the commercial dry powder. Both are approximately 90% active.

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EXAMPLE 9

An important advantage of glyphosate WSP formulations over the commercially available aqueous Roundup formulation is the ability to incorporate solid additives including illustrative types which have been enumerated previously. Water-insoluble liquid additives, in small quantity or absorbed on a carrier can also be used. Example 9 also shows a number of examples of additives combined with WSP containing various acid acceptors.

EXAMPLE 2GLYPHOSATE WSP CONTAINING ADDITIVES

<u>ADDITIVE, %</u>	<u>ACID ACCEPTOR, %</u>	<u>% GLYPHOSATE(99.6%)</u>	<u>SURFACTANT, %</u>
ammonium sulfate, 76.14	sodium acetate, 5.85	11.65	Sellogen HR (75%), 6.36
" 77.75	sodium carbonate, 3.86	11.90	Witconate AOS***, 6.49
" 76.57	sodium thiosulfate.5 H <sub>2</sub> O 5.31	11.72	" " 6.40
" 76.03	sodium bicarbonate, 5.98	11.63	" " 6.35
" 76.14	tripotassium phosphate, 7.54	11.44	" " 6.25
" 77.14	sodium sulfite 4.62	11.80	" " 6.44
" 75.85	trisodium phosphate, 6.22	11.60	Witconate AOS 6.33
" 76.42	sodium formate, ** 4.92	11.70	" " 6.47
" 69.81	sodium hydroxide (76%), 5.12	16.36	" AOK 8.71
ammonium chloride 72.03	" " 5.85	13.92	" " 7.70
oxalic acid·H <sub>2</sub> O 32.84	trisodium phosphate 17.75	32.99	" " 6.42

\* H<sub>2</sub>S odor present indicating decomposition of the thiosulfuric acid formed.

\*\* Formulation contains 0.5% SWS-131 defoamer.

\*\*\* Dried to give 90% powder.

Combinations of glyphosate WSPs and water insoluble co-herbicides can be accomplished using finely powdered co-herbicides or co-herbicides as WDG formulations. Co-herbicides could be either liquids or solids as WDGs and could include alachlor, atrazine, MON 097, Dual, Goal, Whip, actives, etc. Solid actives such as Oust, Glean, diuron, simazine, atrazine, Wlly, Classic, etc. could be incorporated in the WSP as fine powders.

A glyphosate/alachlor formulation was prepared by blending an alachlor water dispersible granule (67%) with glyphosate WSP based upon sodium hydroxide and Witconate AOK or Sellogen HR.

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Combinations of glyphosate WSPs and water insoluble co-herbicides can be accomplished using finely powdered co-herbicides or co-herbicides as WDG (water dispersible granules) formulations. Co-herbicides can be either liquids or solids as WDGs and can include alachlor, atrazine, MON-097, Dual, Flex, Goal, Whip, actives, etc. Solid actives such as Oust, Glean, diuron, simazine, atrazine, Ally, Classic, etc. can be incorporated in the WSP as fine powders. A dispersing agent may be beneficial in the latter formulations.

A glyphosate/alachlor formulation was prepared by blending an alachlor WDG (67% active) with WSPs based upon sodium hydroxide and witconate AOK or Sellogen HR. The formulations were as follows:

20	<u>INGREDIENTS</u>	<u>A</u>	<u>B</u>
	Glyphosate (95.8%)	54.19	51.23
	Sodium hydroxide (76%)	16.79	16.04
	Witconate AOK (90%)	28.84	-----
25	Sellogen HR (75%)	-----	32.73

The following blends were prepared and added to 40 ml of water, stirred and poured into small diameter, 50 ml Nessler tubes and inverted 10 times to give the following results:

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<u>SAMPLE</u>	<u>INITIAL APPEARANCE</u>	<u>1 Hr</u>	<u>24 Hr</u>	<u>REDISPERSE</u>
D. 1.55 g A 2.00 g WDG	Homogeneous	Trace Sediment	4mm sed., clear solution	2 inversions required
E. 1.63 g B 3.00 g WDG	"	2 mm Sediment	" "	15 inversions required
F. 3.00 WDG	Very Flocculated	9 mm Loose Sediment	" "	No redispersion in 15 inversions

**TABLE II**  
**COMPOSITION OF SURFACTANTS**

Morwet B (75%)	sodium n-butylphenylthale sulfonate	
Morwet DB (75%)	sodium dibutylphenylthale sulfonate	
Morwet EFW (94%)	blend of alkylphenylthale sulfonate and a sulfonated carboxylate	
Morwet IP (75%)	sodium diisopropylphenylthale sulfonate	
Morwet M (96%)	sodium mono and dimethylphenylthale sulfonate	
Sellogen HR (75%)	sodium diisopropylphenylthale sulfonate	
Witconate KAS-10 (90%)	- Witco EXP 5093-15C, Potassium decyl sulfonate	
Sodium dodecyl sulfonate (90%)	- prepared from the corresponding IPA salt (Witco EXP 4896-9)	
Potassium tetradecyl sulfonate(90%)	- prepared from the corresponding IPA salt(Witco EXP 4896-10)	13
Sodium tetradecyl sulfonate(90%)	- prepared from the corresponding IPA salt (Witco EXP 4896-10)	6
Witconate NAS-1416 (90%)	- Witco EXP 5093-15D, (mixture of sodium tetradecyl and hexadecyl sulfonate)	
Witconate KOAS-10 (90%)	- Witco EXP 5093-15A, potassium decyl alpha-olefin sulfonate	
Witconate AOS-12 (90%)	- Witco EXP 5042-87B, sodium dodecyl alpha-olefin sulfonate	
Witconate KOAS 14-16 (90%)	- Witco EXP 5093-15B, potassium tetradecyl and hexadecyl-alpha-olefin sulfonate	
Witconate AOK (90%)	- sodium tetradecyl and hexadecyl alpha-olefin sulfonate (dry form of Witconate AOS)	
Aerosol OTB (100%)	- Na dioctylsulfosuccinate/benzoic acid complex	
Igepon T-77 (67%)	- Sodium N-methyl-N-oleyl taurate	

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EXAMPLE 11

The foll wing master batches were prepared from minus 50 mesh ingredients.

5

<u>INGREDIENTS</u>	<u>A</u>	<u>B</u>
Glyphosate (99.,5%)	70.72	75.47
Sodium oxalate	29.25	----
10 Sodium hydroxide (76%)	----	24.53
	100.00	100.00
% glyphosate present	70.68	75.43

15            Spray solutions for bioassays to compare the effectiveness of the various surfactants were prepared by adding the desired weights of master batch and surfactant to give an N-phosphonomethylglycine surfactant ratio of 2:1. The bioassay results are  
20 provided in Example 12.



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EXAMPLE 12BIOLOGICAL EVALUATION OF DRY SURFACTANTS  
FOR USE WITH WSP FORMULATIONS

5	<u>Surfactant</u> <u>Treatment**</u>	<u>% INHIBITION*</u>	
		<u>Sodium</u> <u>Oxalate***</u>	<u>Sodium</u> <u>Hydroxide****</u>
10	Witconate AOK	61.7	24.4
	Morwet B	35.0	13.3
	Morwet DB	50.0	22.8
	Morwet EFW	11.7	7.8
	Morwet IP	43.7	21.1
15	Morwet M	16.1	15.6
	Sellogen HR	42.2	13.3
	Witco KAS-10	49.7	22.2
	Witco C <sub>14</sub> SO <sub>3</sub> K	43.0	7.8
	Witco C <sub>14</sub> SO <sub>3</sub> Na	22.8	12.2
20	Witco KAOS-10	49.4	27.2
	Witco KAOS-12	40.0	47.8
	Witco KAOS 14-16	57.8	27.2
	Untreated Check	0	0

25

\* Means of 3 rates (1/4, 1/2, 3/4 pound per acre of glyphosate) (0.28, 0.56, 0.84 kg/ha) against Johnsongrass four weeks after treatment.

\*\* All surfactants were added to give 0.5% of 100% surfactant.

30 \*\*\* % inhibition for formulations based on sodium oxalate as the acid acceptor.

\*\*\*\* % inhibition for formulations based on sodium hydroxide as the acid acceptor.

35

EXAMPLE 13

Witconate AOK and Sellogen HR were used as surfactants for field testing glyphosate WSP formulations. Field test plots of 10x25 ft. (3.05 x 7.62 meters) replicated three times using a randomized complete block design at 10 locations were sprayed using a tractor-mounted sprayer calibrated to apply 10 gallons/acre (94 liters/hectare) of the aqueous solutions of the WSPs at several concentrations of glyphosate. The components of the formulations field tested were as follows:

<u>CODE</u>	<u>ACID ACCEPTOR</u>	<u>SURFACTANT</u>	<u>CO-HERBICIDE</u>	<u>ADDITIVE</u>
245	Sodium oxalate	Witconate AOK	-----	-----
246	"	Sellogen HR	-----	-----
247	Sodium Hydroxide	Witconate AOK	-----	-----
248	"	Sellogen HR	-----	-----
249	"	Witconate AOK	-----	Ammonium sulfate
250	"	"	2,4-D	-----
251	"	"	"	Ammonium sulfate
252	"	"	Dicamba	-----
253	"	"	"	Ammonium sulfate
312	"	Witconate AOS-12	-----	-----

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EXAMPLE 14

The composition of the field test formulations  
follow:

	5	CODE	INGREDIENTS	%	WEIGHT/ GRAMS
		245	Glyphosate (95.8%)	51.79	1420.5
			Sodium oxalate	20.64	566.2
			Witconate AOK (90%)	27.57	756.0
10		246	Glyphosate (95.8%)	49.08	1420.6
			Sodium oxalate	19.56	566.2
			Sellogen HR (75%)	31.36	907.4
15		247	Glyphosate (95.8%)	54.19	1420.5
			Sodium hydroxide (76%)	16.79	444.7
			Witconate AOK (90%)	28.84	756.0
		248	Glyphosate (95.8%)	51.23	1420.5
20			Sodium hydroxide (76%)	16.04	444.7
			Sellogen HR (75%)	32.73	907.4
		249	Glyphosate (95.8%)	16.36	1420.5
			Sodium hydroxide (76%)	5.12	444.7
25			Witconate AOK (90%)	8.71	756.0
			Ammonium sulfate	69.81	6059.8
		250	Glyphosate (95.8%)	18.47	1420.5
			2,4-D (97%)	32.43	2494.0
30			Witconate AOK (90%)	34.95	2688.0
			Sodium hydroxide (76%)	14.15	1088.0
		251	Glyphosate (95.8%)	10.33	1420.5
			2,4-D acid) (97%)	18.14	2494.0
35			Witconat AOK (90%)	19.55	2688.0
			Sodium hydroxide (76%)	7.91	1088.0
			Ammonium sulfate	44.07	6059.8

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252	Glyphosate (95.8%)	23.85	1420.5
	Dicamba (88%)	18.54	1104.1
	Witconate AOK (90%)	45.18	2691.3
	Sodium hydroxide (76%)	12.43	740.4
5			
253	Glyphosate (95.8%)	11.82	1420.5
	Dicamba (88%)	9.19	1104.1
	witconate AOK (90%)	22.40	2691.3
	Sodium hydroxide (76%)	6.16	740.4
	Ammonium sulfate	50.43	6059.8
10			
312	Glyphosate (95.8%)	54.19	143.74
	Sodium hydroxide (76%)	16.97	45.01
	Witconate AOS-12 (90%)	28.84	76.50
15			

Summaries of the field test data are presented in

20 EXAMPLES 15 AND 16. The WSPs based on Witconate AOK and sodium oxalate are equivalent to commercial Roundup. The sodium hydroxide /Witconate AOK/ammonium sulfate WSP was equivalent to the Roundup/ammonium sulfate tank mix. The glyphosate/2,4-D WSP was less active than Landmaster

25 whereas when both formulations contained ammonium sulfate, they were equivalent. Similar results were obtained with the dicamba systems.

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EXAMPLE 15FIELD TEST RESULTS FOR GLYPHOSATE  
WATER SOLUBLE POWDER (WSP) FORMULATIONS

5	<u>TREATMENT</u>	<u>% CONTROL*</u>	
		<u>Grasses</u>	<u>Broadleaves</u>
	Roundup (As Comparative)	74	61
	Glyphosate/Sellogen		
10	Sellogen/sodium oxalate WSP	71	59
	Glyphosate/AOK/ sodium oxalate WSP	79	66
15	Glyphosate/ Sellogen/NaOH WSP	58	43
	Glyphosate/ AOK/NaOH WSP	69	58
20	Roundup/AS** (As Comparative)	82	75
25	Glyphosate/ AOK/NaOH/AS WSP	82	77

\* Average of plots at multiple locations

\*\* Ammonium sulfate was added to a tank mix of Roundup.

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EXAMPLE 16FIELD TEST DATA FOR PACKAGE MIX WSP FORMULATIONS

5	<u>TREATMENT</u>	<u>% CONTROL*</u>	
		<u>Grasses</u>	<u>Broadleaves</u>
	LANDMASTER**	81	86
	GLYPHOSATE/2,4-D WSP	76	75
	LANDMASTER/AS	84	89
	GLYPHOSATE/		
10	2,4-D/AS/WSP	84	90
	MON-8778***	82	73
	GLYPHOSATE/DICAMBA WSP	73	58
	MON 8778/AS	84	79
	GLYPHOSATE/DICAMBA/AS WSP	83	79

15

\* Average of plots at multiple locations

\*\* Commercial aqueous formulation of glyphosate and  
2,4-D

\*\*\* Aqueous Roundup herbicide/dicamba tank mix

20

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EXAMPLE 17

A premix powder formulation was prepared according to the following formulation:

5	<u>Ingredients:</u>	<u>Weight (Grams)</u>	<u>Percent by Weight</u>
	Glyphosate acid (dried)	6205.0	62.05
	96.7% ae.		
	Sodium bicarbonate	3345.0	33.45
10	Sodium Sulfite	40.0	0.40
	Sag 47 Defoamer	10	0.10
	PEG 3350	400.0	4.00
	Carbowax 3350		
	Total	10000.0	100.00%
15			

Glyphosate acid was substantially unreacted. This means that glyphosate is applied to plants as glyphosate acid if no water is added to the formulation of this invention. If water is added, it is believed that glyphosate reacts with the acid acceptor and some glyphosate salt is formed.

This premix powder was processed into water soluble granules (WSG) by first compacting the pre-mix powder into wafer shape using a roller compactor called a Chilsonator. This roller compactor employed pressures of about 4000 pounds per square inch ( $27.6 \times 10^3$  kilo Pascals). The wafers from this Chilsonator were then ground to about 12 mesh or less using a Straub 4E grinder (similar to a grist mill, although a Fitz mill is preferred). The powder from the Straub grinding process was screened off and recycled again through the Chilsonator. The process of using the Chilsonator and the Straub grinder was repeated until a desired amount of granules were made.

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The powder prepared in the immediately described process above was fed into a hopper and then using a volumetric feed system was fed into a dye/punch/mold arrangement for formation into tablets. Pressure was applied to the punch and dye and tablets were formed. The pressure was removed and the tablets were ejected. The tablets weighed about 4.5 grams plus or minus 0.2 gram. The tablets were about 0.75 inch (1.91 cm) in diameter and about 0.5 inch (1.27 cm) in height. Tablets of different weights and configurations can also be made using this process.

#### EXAMPLE 18

Glyphosate acid technical (43% w/w), a propoxylated quaternary ammonium surfactant (15% w/w) known as Dodigen 4022 and ammonium sulfate 97% (30% w/w) are mixed in a planetary mixing equipment until a homogeneous dough is obtained. Sodium carbonate (12% w/w) is then added to the dough which is quickly homogenized and immediately pelleted by an extruder before being dried in a fluid bed dryer. The final composition of the extruded granules obtained after the extrusion step contains 1% w/w of water.

The extruded granules are poured into the spray tank filled with water. The neutralization of glyphosate by sodium carbonate, then occurs and the effervescence due to the release of CO<sub>2</sub> in the solution makes the extruded granules dissolve in less than 1 minute with no external agitation. As a matter of comparison, similar granules with no effervescence do not really dissolve with no external mixing and under agitation take between 2 to 4 minutes to dissolve the actual time taken depending on the turbulence in the spray tank.



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An important advantage of these glyphosate WSP formulations is their ability to include solid additives. One of the most important solid additives is ammonium sulfate which can be included in the WSP at any  
5 desired level. Ammonium sulfate contributed increased biological activity as is shown in Examples 15 and 16. Ammonium sulfate is only compatible to a low degree in an aqueous glyphosate/surfactant formulation. Ammonium sulfate is also an effective solid additive in  
10 glyphosate WSP package mixes with co-herbicides which form water soluble salts as shown in Example 16.

Particle size of the WSP or WSG products of this invention can be varied as long as the product is  
15 completely dissolved prior to application by spraying. The preferred mode of manufacture of the glyphosate WSPs involves grinding the individual ingredients using conventional equipment and blending using such equipment as a ribbon-or V-blender or grinding the blended  
20 ingredients. Since many of the surfactants and some of the acid acceptors are very hygroscopic, all operations are preferably carried out in closed equipment and moisture-proof packaging is required such as polyethylene or polyethylene laminated paper bags or the  
25 like. A particularly preferred type of packaging is a water soluble bag within an outer moisture proof container or bag.

If desired, the powdered products of this  
30 invention may be compacted by various means as further exemplified in Example 17 and then ground and sieved to give a granular product. It may be desirable to incorporate a gas-forming ingredient to give more rapid disintegration and solution of the granular product.

35

If desired, alternate carbonates may be employed such as potassium bicarbonate, sodium or potassium

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carbonate, mixtures thereof and the like or alkaline earth metal carbonates or bicarbonates, mixtures thereof and the like.

- 5           If desired alternate sulfites may be employed such as potassium sulfite or an alkaline earth metal sulfite.

- Alternate lubricants may be employed including  
10 PEG's of varying molecular weight, methyl stearate or magnesium stearate, mixtures thereof and the like. Alternate defoamers may be employed such as AntiFoam® 30 IND.

- 15           A binder can be employed, such as PVP, if desired although such use is optional.

- The use of a small percentage of a carbonate-based acid acceptor (a carbonate such as sodium  
20 bicarbonate/sodium carbonate, ammonium bicarbonate, mixtures thereof and the like) in the WSG formulation which in the presence of water will give off carbon dioxide which will increase the rate of solution by rupturing granules.

25

- The WSP or WSG compositions of this invention may vary widely with regard to the ratios of ingredients. If a surfactant is employed a glyphosate/surfactant ratio of about 4:1 to about 1:2 is a preferred range;  
30 however, other ratios, including a 1:0 may be used. The latter formulation may find utility where the presence of a surfactant is unnecessary or undesirable. The ratio of glyphosate to acid acceptor depends on the useable equivalent weight of the acceptor as shown in  
35 Table I. One useable equivalent of acid acceptor to one mole of glyphosate is required to provide for solution of the glyphosate. Usually, a 2-5% excess of acid

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acceptor is employed since acidic by-products in commercial glyphosate necessitate a slight excess. Depending on the use of the WSP or WSG, that is, the volume of water used in the spray, less than the  
5 theoretical quantity of useable equivalent of acid acceptor may be sufficient since glyphosate is soluble in water to the extent of about 1.0 wt. % at 25°C. WSP and WSG formulations generally are not detrimentally affected by pressure and/or temperature variations. As  
10 mentioned previously, moisture is a major concern in processing and storage of dry glyphosate formulations because of the hygroscopic nature of some of the ingredients, especially the surfactant.

15 In practicing the present method of-use of a dry glyphosate-containing formulation to kill or control weeds the best mode involves addition to water of a herbicidally effective amount of the composition of this invention followed by application via spraying or one of  
20 the many known wiping techniques to the locus of the plants to be killed or controlled. Addition of water may not be required (but is recommended) when application is made to plants having excessive dew. Application of a composition of this invention is made  
25 so that the plant is contacted with a herbicidally effective amount of N-phosphonomethylglycine.

Many acid acceptors are operable in the present invention, however, sodium oxalate and sodium  
30 bicarbonate are preferred and sodium bicarbonate is most preferred.

Many solid surfactants can be used in glyphosate WSPs or WSG's, however, sodium tetradecyl/hexadecyl  
35 alpha-olefin sulfonate (Witconate AOK) is preferred. In formulations with low surfactant content, say about 2-5%, a liquid ethoxylated tallow amine surfactant is

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preferred due to its high potentiating effect n  
glyphosate activity. With the propoxylated quaternary  
ammonium surfactants, one may use up to 15% by weight.

5 In summary, the advantages of the dry glyphosate  
based formulations over the current aqueous formulations  
include higher active (glyphosate) content,  
compatibility with solid or water-insoluble liquid  
additives, compatibility with solid and liquid water  
10 insoluble co-herbicides as powders or water soluble  
granules, use of lower cost packaging and eliminating  
the necessity of manufacturing a glyphosate salt prior  
to formulation of the final commercial product.

15 Although this invention has been described with  
respect to specific embodiments, the details hereof are  
not to be construed as limitations, for it will be  
apparent that various equivalents, changes and  
modifications may be resorted to without departing from  
20 the spirit and scope of this invention. It is  
understood that such equivalent embodiments are intended  
to be included within the scope of this invention.

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## WHAT IS CLAIMED IS:

1. A substantially dry, water soluble or dry, water dispersible agriculturally acceptable composition comprising a herbicidally effective amount of substantially non reacted N-phosphonomethylglycine, and an acid acceptor.
2. The composition of Claim 1, which further comprises a solid or liquid surfactant in an amount of about 0.2 to about 15.0% by weight.
3. The composition of Claim 2 wherein said dry composition is a water soluble or dispersible powder, a water soluble or dispersible granule, a water soluble or dispersible tablet or a water soluble or dispersible briquette.
4. The composition of Claim 1 wherein the amount of water in said dry composition is in the range from about 0.01 to about 10.0 percent by weight of the total composition.
5. The composition of Claim 4 wherein said amount of water in said dry composition is in the range from about 0.2 to about 2.0 percent by weight of the total composition and said composition is in a granular form.
6. The composition of Claim 1 wherein said acid acceptor is selected from the group consisting of ammonium and alkali metal carbonates, bicarbonates, acetates, meta borates, citrates, formates, oxalates, phosphates, propionates, pyrophosphates, metasilicates, orthosilicates, sulfites, thiosulfates, tetraborates, tripolyphosphates, m taphosphat , sodium hydroxide,

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potassium hydroxide, tetrasodium EDTA, and mixtures  
ther of.

7. The composition of Claim 1 which further  
5 comprises a co-herbicide.

8. The composition of Claim 1 or Claim 7 which  
further comprises a dispersing agent or a corrosion  
inhibitor.

10

9. The composition of Claim 1 or Claim 7 which  
further comprises a thickener.

10. The composition of Claim 1 or Claim 7 which  
15 further comprises a calcium sequestrant and/or a  
defoamer.

11. The composition of Claim 1 or Claim 7 which  
further comprises an agriculturally acceptable ammonium  
20 salt or other synergist.

12. The composition of Claim 1 or Claim 7 which  
further comprises a quick-burn additive.

13. The composition of Claim 1 or Claim 7 which  
25 further comprises a humectant.

14. The composition of Claim 1 or Claim 7  
further comprises a dye or pigment.

30

15. The composition of Claim 6 or Claim 7  
wherein said co-herbicide forms a water soluble salt.

16. The composition of Claim 7 wherein said  
35 co-herbicide is selected from the group consisting of 2,  
4-D (2,4-dichlorophenoxy)acetic acid), dicamba, (3,6-  
dichloro-p-anisic acid), picloram (4-amino-3,5,6-tri-

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chl ropyridine-2-carboxylic acid), MCPA (4-chloro-*o*-  
 tolyloxyacetic acid), bialaphos (DL-homoalanin-4-yl-  
 methylphosphinate), imazaquin, (2-[4,5-dihydro-4-methyl-  
 4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinoline-  
 5 carboxylic acid), dalapon (2,2-dichloropropionic acid),  
 dichlorprop 2-(2,4-dichlorophenoxy)propionic acid), MCPB  
 (4-(4-chloro-*o*-tolylloxy)butyric acid, acifluorfen (5-  
 (2-chloro-4-(trifluoromethyl)phenoxy-2-nitrobenzoate),  
 chloramben (3-amino-2,5-dichlorobenzoic acid), endothall  
 10 (7-oxabicyclo(2.2.1)heptane-2,3-dicarboxylic acid),  
 2,4,5-T (2,4,5-trichloroacetic acid), 2,3,6-TBA (2,3,6-  
 trichlorobenzoic acid), glufosinate-ammonium (3-amino-  
 3-carboxypropyl)-methylphosphinate), imazapyr (2-[4,5-  
 dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-  
 15 2-yl]-3-pyridinecarboxylic acid), and mixtures thereof.

17. The composition of Claim 7 wherein said  
 co-herbicide is essentially water insoluble.

20 18. The composition of Claim 17 wherein said  
 water insoluble co-herbicide is present in said water  
 dispersible composition as a fine powder.

19. The composition of Claim 17 wherein said  
 25 water insoluble co-herbicide is a liquid or a solid  
 present in said composition as a water-dispersible  
 granule and selected from alachlor (2-chloro-2',6'-  
 diethyl-N-methoxymethylacetanilide), atrazine (2-  
 chloro-4-ethylamino)-6-(isopropylamino)-s-triazine,  
 30 simazine (6-chloro-N,N'di-ethyl-1,3,5-triazine-2,4-  
 diamine, acetochlor (2-chloro-2'-ethyl-6'-methyl-N-  
 ethoxy-methylacetanilide), metolachlor (2-chloro-6'-  
 ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidide),  
 fomesafen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-N-  
 35 (m thylsulfonyl)-2-nitrobenzamide), oxyfluorfen (2-  
 chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoro-  
 methyl)benzene), fenoxaprop-ethylethyl 2,[4-(6-chloro-

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2-benzoxazolyloxy)phenoxy]propanoate), diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea), metsulfuron-methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate), chlorimuron-ethyl ethyl 2-[(4-chloro-6-methoxypyrimidin-2-yl)-amino]carbonyl]amino]sulfonyl]benzoate), linuron 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea), sulfometuron-methyl (2-[3-(4,6-dimethyl-pyrimidin-2-yl)ureidosulphonyl]benzoic acid), chlorsulfuron (1-(2-chlorophenylsulphonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea), and mixtures thereof.

20. The composition of Claim 7, wherein said co-herbicide as a water soluble salt is blended with said composition of Claim 1.

21. The composition of Claim 1 wherein said surfactant comprises a nonionic surfactant, an anionic surfactant, a cationic surfactant, an amphoteric surfactant, or mixtures thereof.

22. The composition of Claim 21 wherein said nonionic surfactant is a polyoxyethylene polyoxypropylene block copolymer, an alkyl phenol polyoxyethylene ether, a polyoxyethylene oleyl ether, or mixtures thereof.

23. The composition of Claim 21 wherein said anionic surfactant is sodium laurylsulfate, a sodium alpha-olefin sulfonate, a potassium alpha-olefin sulfonate, a sodium alkane sulfonate, a potassium alkane sulfonate, an ammonium alkane sulfonate, an isopropylammonium alkane sulfonate, a sodium alkyl, or dialkyl naphthalene sulfonate or mixtures thereof.

24. The composition of Claim 21 wherein said cationic surfactant is an ethoxylated fatty amine, an



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amine oxide, such as lauryl dimethylamine oxide, N,N-bishydroxyethylcocoamine oxide, a propoxylated quaternary ammonium compound, or mixtures thereof.

5           25. The composition of Claim 1 wherein N-phosphonomethylglycine is in the form of a water soluble salt selected from the group consisting of the ammonium, isopropylamine, trimethylsulfonium, iminourea, potassium, sodium salts, or mixtures thereof.

10

26. A dry water soluble composition comprising said composition of Claim 25 and further comprising ammonium sulfate, potassium sulfate, potassium chloride, sodium sulfate, urea, mixtures thereof and the like.

15

27. A process for preparing a dry, water soluble agriculturally acceptable composition which comprises admixing ingredients N-phosphonomethylglycine, an acid acceptor, optionally a solid or liquid surfactant, and  
20 thereafter blending said admixed ingredients to form said composition or compacting or tabletting said composition to form a granule.

28. A method of killing or controlling weeds  
25 using the composition of Claim 1 by applying a herbicidally effective amount of glyphosate to the locus of the plant or weed to be killed or controlled.

29. The process of Claim 28 wherein a  
30 co-herbicide is admixed with said N-phosphonomethylglycine, said acid acceptor, and optionally said solid or said liquid surfactant.

30. The method of killing or controlling weeds  
35 of Claim 29, which further comprises admixing said composition in the form of a tablet, briquette, powder or granule or mixture thereof with water and applying a

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herbicidally effective amount to the 1 cus of the plant  
or weed to be killed or controlled.

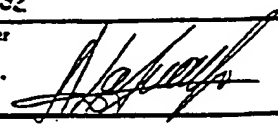
31. A tablet, briquette, powder or granule  
5 having the composition of Claim 1.

32. A tablet of Claim 31, wherein said tablet is  
water soluble and is about 2 inches (5.08 centimeters)  
long by about 1/2 inch (1.27 centimeters) wide by about  
10 1/2 inch (1.27 centimeters) thick.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/00274

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 A01N57/20;      //(A01N57/20,25/14, 25/12)		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claims No. <sup>13</sup>
X	WORLD PATENTS INDEX LATEST Week 8736, 1 August 1987 Derwent Publications Ltd., London, GB; AN 87-253854 & JP,A,62 175 408 (ISHIHARA SANGYO KAISHA) see abstract ---	1-32
X	WO,A,9 007 275 (MONSANTO COMPANY) 12 July 1990 see examples 8,16-23 see claims ---	1,25,26
X	EP,A,0 360 441 (E.I. DU PONT DE NEMOURS AND COMPANY) 28 March 1990 see page 9, line 40 see page 16, line 24 - line 27 see claims 1-3,10 --- -/-	1-32
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
2      19 MAY 1992	23.06.92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DALKAFOUKI A. 	

(CONTINUED FROM THE SECOND SHEET)

Form PCT/ISA/210 (extra sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9200274  
SA 57070**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 19/05/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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		CA-A-	2006816	30-06-90
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		EP-A-	0452366	23-10-91
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EP-A-0360441	28-03-90	AU-A-	4193689	02-04-90
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